Research Communications

Perchlorate Identification in Fertilizers

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Perchlorate has contaminated groundwater, drinking
water, and soils at several locations in the United States.
The primary source of contamination at sites that have
been investigated to date seems to be from industrial and
military operations that use perchlorate as an oxidizing
agent. However, recent examination of several fertilizers
and fertilizer components showed that perchlorate is present
at levels up to 0.84 wt %. These preliminary results
suggest that fertilizers could be a source for perchlorate
accumulation in the food chain.

Introduction

Perchlorate is commercially produced as solid salts of
ammonium, sodium, and potassium cations; it is used as an
oxidizer in solid propellants for rockets, missiles, fireworks,
and certain munitions and used in the manufacture of
matches. Potassium perchlorate has, in the past, been used
therapeutically to treat hyperthyroidism resulting from
Graves' disease (1). Perchlorate is water-soluble, exceedingly
mobile in aqueous systems, and can persist for many decades
under typical groundwater and surface water conditions (2).
Perchlorate is of concern because of uncertainties about
toxicity and health effects at low levels in drinking water,
impact on ecosystems, and indirect exposure pathways for
humans due to accumulation in vegetables. Perchlorate has
been found in the water resources of several western states,
including Lake Mead and the Colorado River, in the range
from 4 to 16 μg/L (2). This water is used for drinking, irrigation,
and recreation for approximately half of the population in
Arizona, California, and Nevada. Currently, an action level
of 18 μg/L has been adopted by several affected states.

The use of Chilean saltpeter as a fertilizer was a common
practice with rye crops several decades ago. Occasionally
observed damage to the crops was attributed to the potassium
perchlorate present as a contaminant in the saltpeter, which
contains up to 1.5 wt % of perchlorate (3). Tollenaar and
Martin (4) reported that Chilean nitrate was observed to cause
leaf rugosity in soybean plants when applied as a fertilizer.
Although Chilean nitrate is not a major component of modern
agricultural fertilizers, these results (4) indicated that per-
chlorate may have been and still may be present in the
horticultural fertilizers used on lawns and gardens in the
United States.

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This work presents the results of a screening study to
identify and quantify perchlorate in mineral deposits and in
some garden and crop fertilizers that are currently and
regularly used throughout the country. Phosphate rock
samples and dihydrogen ammonium phosphate were pur-
chased from the National Institute of Standards and Tech-
nology (NIST), and potash samples were provided by the Air
Force Restoration Division at Wright-Patterson Air Force Base
from the mineral archives of the U.S. Geological Survey. We
also analyzed a total of nine fertilizers, purchased from local
stores in Athens, GA, containing various ratios of nitrogen,
phosphate, and potassium (N:P:K). The two ammonium
nitrate fertilizers are process-derived from nitrogen in the
atmosphere, whereas the other seven are manufactured from
natural potassium deposits most likely langbenite from New
Mexico.

Sample Preparation. Fertilizer samples were prepared
by dispersing (or, in the case of ammonium nitrate, dissolving)
5 g of the solid fertilizer in 45 mL of deionized water with
shaking every 4 h for 48 h of dissolution time. Except for
ammonium nitrate, all the fertilizer sample was not dissolved
in water. A 2-mL sample of each fertilizer solution was
centrifuged at 7000 rpm for 10 min. An aliquot of the
supernatant was diluted 10–100 times to reduce the effect
of total dissolved solids in the analysis by ion chromatography
(IC). For capillary electrophoresis (CE), 2 mL of the centri-
fuged supernatant was diluted to 100 or 1000 mL, depending
on the concentration of perchlorate.

Samples of fertilizers for Raman analysis were prepared
in the same manner, except that the 5 g of solid fertilizer was
placed in only 20 mL of water. After centrifugation, about 0.1
g of activated charcoal was placed in approximately 10 mL
of the supernatant and manually shaken for about 1 min.
The sample was then filtered with a 0.2-μm nylon syringe
filter. This is a commonly employed technique for removing
highly flourescent, trace level impurities that can interfere
with Raman spectral analysis.

Analytical Methods. The principal method for detection
of perchlorate in fertilizers employed a Dionex 500 ion
chromatograph. The system includes an LC20 chromatograph
enclosure, a CD20 conductivity detector, a GP40 gradient
pump, and an AS3500 autosampler. The GP40 gradient pump
was operated in an isocratic mode to enhance baseline
stability. All standards and solutions were made with 18 MΩ
Milli-Q water. The perchlorate standards were made from
reagent-grade sodium perchlorate (Aldrich Chemical Co.).
The following parameters were selected to analyze the
fertilizer samples: (i) an anion self-regenerating suppressor
II (4 mm) with a current setting of 300 mA, operated in the
external mode of suppression, with 18 MΩ Milli-Q water
utilized as the regenerant and pressurized to 25 psi to ensure
a 3 mL/min flow rate; (ii) the columns employed were a
Dionex IonPac AG11 (4 × 50 mm) and a Dionex IonPac AS11
analytical (4 × 250 mm); (iii) the detector temperature was
set to ambient; (iv) the sample loop size was 100 μL; (v) the
eluent was 100 mM sodium hydroxide in Milli-Q water that
was degassed for 10 min prior to the addition of the solute,
with a flow rate of 1.0 mL/min. These parameters resulted
in elution of the perchlorate in approximately 12 min, with
a total run time of 15 min. Six standard perchlorate
concentrations of 0–20 mg/L were used for method calibra-
tion. Dionex PeakNet software V4.3 was used in data
collection and method control, with a plot scale setting of
9 μS maximum and −3.0 μS minimum. The detection limit

of the IC method was 10 μg/L. The concentration of perchlorate was calculated based on the area of the peak. Six replicate measurements were made for each fertilizer and fertilizer component.

Capillary electrophoresis was used to confirm the ion chromatographic measurements of perchlorate anion in the fertilizer samples. Pyromellitic acid was used as the visualization reagent for indirect detection, and a glycerol-coated column was used for reduction of electroosmotic flow. Conditions were as follows: (i) instrument: Beckman P/ACE 5000 with Beckman System Gold software; (ii) column: CE 200/Glycerol (Isco, Inc.), which is a fused-silica column, 47 cm total length, 40 cm to the detector, 300 μm o.d., and 75 μm i.d., in which the silica groups had been reacted with glycerol; (iii) instrument conditions: column temperature of 25 °C, voltage at 20 kV with polarity reversed (detection at anode), and hydrodynamic sample injection over 5 s; (iv) detector: UV/vis, monitored at 254 nM; (v) background electrolyte: 40 mM phosphate at pH 7.0 containing 2.24 mM pyromellitic acid. After each sample analysis, the column was washed with water for 5 min and then with buffer for 4 min before the next sample was injected. Standard aqueous (deionized water) solutions of 25–1000 mg/L of sodium perchlorate were used to prepare a standard curve. Each solution was analyzed twice, and the resulting absorbance values were averaged; the correlation coefficient for regression of the averaged values was 0.9932. The limit of detection for perchlorate was approximately 10 mg/L in the injected sample. Migration times for the perchlorate peak in all 14 analyses used for the standard curve ranged from 2.93 to 3.04 min, with a relative standard deviation of 1.1%. This precision readily allowed selection of the perchlorate peaks in the fertilizer samples. In several samples, peak identities were checked by spiking the sample with a known concentration of perchlorate standard and observing the increase in peak area with no peak splitting.

Although agreement among two independent chromatographic/electrophoretic techniques provides reasonable confidence in the perchlorate identification, we sought to further increase our confidence level by analysis with an information-rich spectroscopic technique. To this end, we measured the Raman spectrum of the aqueous fraction of each fertilizer individually dispersed in water and compared those spectra to the Raman spectrum of ammonium perchlorate dissolved in water. The spectra were acquired with a Kaiser Optical Systems HoloProbe, using 785 nm laser excitation from an SDL-8530 external cavity stabilized diode laser. This type of Raman instrument has been fully described elsewhere (5). Briefly, light from the laser was coupled to a remote probe head via a 1.9 m long fiber optic cable. The laser light was brought to focus with a series of lenses at approximately 2.5 in. beyond the end of the probe head assembly. A standard glass sample vial containing the aqueous sample was placed in the path of the beam such that the focus of the beam fell in the center of the solution. The power of the laser light at the sample was approximately 95 mW.

Raman scattered light from the sample was collected by the probe head along the same path as the excitation laser beam (i.e., 180° backscattering geometry) and was coupled to a separate 1.9 m long fiber optic cable for delivery to the f/1.8 axial transmissive-type spectrograph. Inside the spectrograph, the Raman scattered light was passed through a holographic notch filter in order to remove elastically scattered laser light returning from the probe head. The Raman scattered light was then focused through a 50-μm slit and directed through a volume holographic transmissive grating. The dispersed Raman spectrum was then focused onto the charge coupled device (CCD) detector, which allowed simultaneous acquisition of the entire Raman
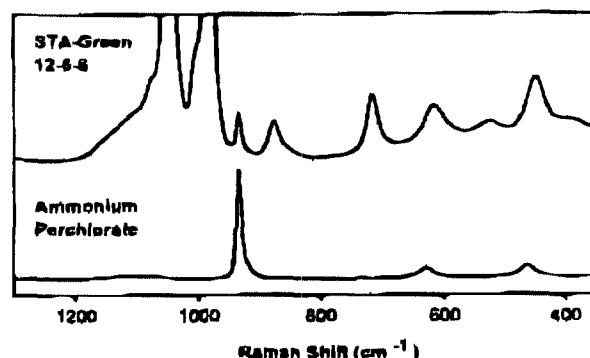
FIGURE 1. Raman spectrum of the STA-Green fertilizer dispersed in water (top) and ammonium perchlorate dissolved in water (bottom). In each case, a Raman spectrum of water has been subtracted from the measured spectrum.

spectrum, with a useable Stokes Raman shift of about 3280–95 cm^{-1}, in a single exposure. The CCD detector used a high quantum efficiency Princeton CCD-1024EHRB back-illuminated, deep-depletion, near-infrared-optimized chip, which was thermoelectrically cooled to −65 °C. Raman spectra measured with this instrument exhibited resolution of about 5 cm^{-1}.

In turn, the Raman spectrum of each of the fertilizers individually dispersed in water was collected, along with a spectrum of 200 mM ammonium perchlorate in water and a spectrum of pure water; each with an exposure time of 20 min. (Thus, a total of 11 spectra were collected.) Each spectrum was frequency corrected based on the previously measured atomic emission lines from a neon bulb. Also, each spectrum intensity was corrected based on a previously measured white light source (i.e., a tungsten bulb) that is assumed to have a flat emission curve in the spectral region of interest. After all spectra were collected, the water spectrum was digitally subtracted from each fertilizer spectrum and from the ammonium perchlorate spectrum. Next, each subtracted spectrum was baseline corrected using multiple fixed points.

The most congested resultant fertilizer spectrum was that of the STA-Green fertilizer (Table 2), which is displayed in the top half of Figure 1. The resultant spectrum for ammonium perchlorate is shown in the bottom half of Figure 1. (Note that the spectra are displayed only over the Raman shift region of 1300–350 cm^{-1}, which is the region that contains peaks attributable to inorganic oxyanions.) The Raman spectrum in the bottom half of Figure 1 is attributable to the perchlorate anion, and the observed peaks have been fully described (6). The most intense peak in the perchlorate spectrum, observed at 934 cm^{-1}, is assigned to v_1, which is the symmetric ClO$_4$ stretching mode. Furthermore, in the perchlorate, spectrum peaks are observed for v_2 at 463 cm^{-1}; v_3 as a weak, broad peak centered at 1113 cm^{-1}; and v_4 at 629 cm^{-1}. The spectrum of the STA-Green fertilizer (top half of Figure 1) is displayed with the most intense peaks off-scale such that the 934 cm^{-1} peak of perchlorate is clearly visible. This peak was observed in the Raman spectrum of each fertilizer sample analyzed. Coupled with the chromatographic data, these observations provide an exceedingly high level of confidence in the identification of perchlorate in all the samples reported in Table 2. The features in the Raman spectrum of the STA-Green fertilizer not attributable to perchlorate arise from the presence of nitrate (the 1048 cm^{-1} peak [off-scale] and the 719 cm^{-1} peak), sulfate (the 981 cm^{-1} peak [off-scale] and the 618 and 449 cm^{-1} peaks), and dihydrogen phosphate (the 878 cm^{-1} peak). Note in the fertilizer spectrum that the 629 and 463 cm^{-1} peaks of perchlorate are only observed as shoulders on the more

TABLE 1. Perchlorate Concentrations in Fertilizer Components

component	perchlorate (%)
phosphate rock (western)[a]	0.10 ± 0.01[c]
phosphate rock (Florida)[a]	0.11 ± 0.02
potash (commercial)[b]	0.29 ± 0.03
potash (muriate)[b]	0.36 ± 0.04
dihydrogen ammonium phosphate[a]	0.46 ± 0.05
urea[d]	0.25 ± 0.02
langbenite[e]	1.86 ± 0.21
Chilean nitrate	3.54 ± 0.34

[a] Samples were purchased from National Institute of Standards and Technology (NIST), Gaithersburg, MD. [b] Commercial source of potash samples. Provided by Greg Harvey, Wright-Patterson AFB, from the mineral archives of the U.S. Geological Survey.. [c] A plus or minus sign (±) indicates the deviation in measurement among the six replicates. [d] Urea sample was purchased from Goldkist, Commerce, GA. [e] TRC, Irvine, CA.

intense, nearby peaks of sulfate.

Results and Discussion

Only ion chromatography was used for quantifying perchlorate in horticultural fertilizer components. The results indicated that all five fertilizer components contained perchlorate ranging between 0.1 and 0.46% levels (Table 1). Dihydrogen ammonium phosphate contained the maximum amount of perchlorate (0.46%) followed by potash samples. Both samples of phosphate rock from Florida and western U.S. contained approximately the same levels (0.10%) of perchlorate, while urea has perchlorate contamination up to 0.25%. Langbenite, the single most important source of potassium sulfate for all major manufacturers has perchlorate up to 1.86%. The results suggest that a source of perchlorate contamination in fertilizers is from mineral deposits that are used in the manufacturing processes.

The results of horticultural fertilizer analyses are summarized in Table 2. Perchlorate was identified in all the fertilizers available for purchase locally, ranging from 0.15 to 0.84 wt %. No apparent correlation between the nitrogen, phosphate, or potassium content and the measured perchlorate levels were observed in the fertilizers except that perchlorate was present even when phosphate and potassium were not. On the bais of the fertilizer component data, it is likely that perchlorate contamination in fertilizers is from the rock deposits and minerals used its manufacture. The use of the CE method was intended to qualitatively confirm the presence of perchlorate, but the methods were also in general quantitative agreement; e.g., for Procare, IC gave 0.20% while CE gave 0.16%; for Scotts winterizer, 0.51 versus 0.62%, and for Premium Lawn, 0.33 versus 0.48%. This general agreement with two different methods indicates that the results are not an artifact of the analysis. This conclusion was also confirmed qualitatively by Raman spectroscopy as described above.

The source of perchlorate in ammonium nitrate and Pennington (both N fertilizers) is unknown. Based on the information provided by the Fertilizer Research Institute (7), "coating" oils used in the manufacture of these two fertilizers may be the primary source of perchlorate contamination. Also, brine solution added during the process for controlling the pH in the final product could be another source of perchlorate in N fertilizers.

The amount of perchlorate introduced into the United States by the application of fertilizer is proportional to usage rates. According to the Fertilizer Research Institute (7), the current world fertilizer consumption is 145.6 million t. Compared to 1994, the consumption in 1996 was up over 8% and includes an increase of 8.5% for nitrogen-based fertilizers. U.S. fertilizer consumption peaked in 1981 at 23.7 million t.

TABLE 2. Perchlorate Concentrations in Commercial Fertilizers[a]

brand/description (N-P-K)	manufacturer/ lot no.	perchlorate (%)
ammonium nitrate 34-0-0	Gold Kist Commerce, GA 20631	0.22 ± 0.04[b]
Lesco 17-3-11	Lesco Rocky River, OH 023-371	0.57 ± 0.03
Procare 10-10-10	Gro Tech Inc. Madison, GA 525-1123	0.20 ± 0.08
fallfeed winterizer 18-6-12	Purcell Industries Sylacauga, AL F 1061-1169	0.15 ± 0.08
STA-Green 12-6-6	Purcell Industries Sylacauga, AL 1061-1324	0.84 ± 0.18
Scotts winterizer 22-4-14	The Scotts Co. Marysville, OH FL 6432037	0.51 ± 0.05
Vigaro 10-10-10	Gro Tec Inc. Madison, GA 525-1123	0.55 ± 0.06
premium lawn 27-2-5	Vigaro Industries Winter Haven, FL 735-8512	0.33 ± 0.08
Pennington 34-0-0	Gro Tech Inc. Madison, GA 525-2043	0.61 ± 0.04

[a] Samples were analyzed by ion chromatography with six independent measurements. Perchlorate given in wt %. [b] A plus or minus sign (±) indicates the deviation in measurement among the six replicates.

On the basis of the application rates (54 lb/ha) recommended on the fertilizer bags and a typical perchlorate concentration of 0.20% observed in this study, it appears that approximately 0.91 kg/ha of perchlorate can be available either for uptake by plants, ion exchange with soils, or transport into the associated groundwaters and surface waters. Currently, research is underway to determine the extent of translocation of perchlorate to root crops, citrus, and leafy vegetables such as lettuce. Clearly, improved knowledge of the potential human exposure to perchlorate through the fertilizer−food chain pathway is warranted based upon the results of this screening study.

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